## Supporting Information

# Secondary Organic Aerosol Formation by Heterogeneous Reactions of Aldehydes and Ketones: A Quantum Mechanical Study

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**Enthalpies of formation**. The ground state energy ($E_{elec}$), the zero point vibrational energy ($E_{zpe}$), the thermal vibrational, rotational, and translational enthalpy from 0 K to 298 K ($\Delta H_{(0\text{-}298K)}$) for the selected 12 compounds are summarized in Table S1. QM heats of formation can be calculated using equation 3 -5 with the information in Table S1. The values are shown in Table S3.

**Table S1: Quantum calculated ground state electronic energies ($E_{elec}$), zero point energies ($E_{zpe}$), and thermal enthalpy from 0 - 298K ($\Delta H_{(0\text{-}298K)}$)**

| | $E_{elec}$ (Hartrees) | $E_{zpe}$ (kcal/mol) | $\Delta H_{(0\text{-}298K)}$(kcal/mol) |
|---|---|---|---|
| Water | -76.44 | 12.48 | 2.37 |
| Formaldehyde | -114.50 | 16.35 | 2.39 |
| Acetaldahyde | -153.82 | 33.46 | 2.95 |
| Acetone | -193.14 | 50.45 | 4.02 |
| Butanal | -232.43 | 68.14 | 4.59 |
| Hexanal | -311.04 | 102.27 | 5.97 |
| Glyoxal | -227.82 | 22.95 | 3.23 |
| Ethylene glycol | -230.25 | 51.80 | 4.02 |
| Hydroxyacetone | -268.36 | 54.10 | 4.55 |
| 2,4-pentanedione | -345.77 | 73.81 | 5.93 |
| Glutaraldehyde | -345.75 | 74.21 | 5.75 |
| Cyclopropane carboxylic acid | -306.46 | 59.06 | 4.25 |

**CHBLC corrections**. However, a direct comparison of QM heats of formation, from Equation 3 – 5, with the experimental values often shows large errors (see Table S3). These errors appear to be highly correlated with the number of carbon or the number of hydrogen atoms in the molecule. Thus, in principle one could attribute the errors in the standard heats of formation to errors in the quantum mechanical ground state electronic energies for the elements. Equation 4 is then changed to:

$$\Delta H^*_{298K} = \sum_{i=1}^{n} n_i [h_i^0 - (h_i^{QM} - \delta h_i^{elec})] \qquad (7)$$

where $\delta h_i^{elec}$ is the enthalpy correction for the i-th element, 0.61, 0.90, and 0.39 kcal/mol for H, C, and O respectively, somewhat higher, 2.84 and 4.80 kcal/mol, for S and N, see Table S2.

**Table S2: Experimental ($h_i^0$) and calculated ($h_i^{QM}$) atomic heats of formation, and the quantum corrections to heats of formation ($\delta h_i^{elec}$)**

| Atom | $h_i^0$ (kcal/mol)[a] | $h_i^{QM}$ (Hartrees)[b] | $\delta h_i^{elec}$ (kcal/mol)[c] |
|---|---|---|---|
| H ($^2$S) | 52.07 | -0.501 | -0.61 |
| C ($^3$P) | 171.18 | -37.841 | -0.90 |
| N ($^4$S) | 112.90 | -54.588 | -4.80 |
| O ($^3$P) | 59.51 | -75.067 | -0.39 |
| S ($^3$P) | 66.20 | -398.086 | 2.84 |

a. The experimental heats of formation, $h_i^0$, and the experimental atomic entropy are taken from NIST database (1).
b. Theoretical atomic heats of formation are calculated at X3LYP/aug-ccpvtz(-f) level
c. Corrections to atomic enthalpies are developed according to Blanco and Goddard (2)

Further corrections can be electron correlated, particularly for valence electrons. A simple classification of valence bond (VB) electron pairs into σ and π electron pairs provides an effective systematic correction, similar to the J2 model. Equation 7 is then changed to:

$$\Delta H^*_{298K} = \sum_{i=1}^{n} n_i[h_i^0 - (h_i^{QM} - \delta h_i^{elec})] + \sigma N_\sigma + \pi N_\pi \qquad (8)$$

where $N_\sigma$ and $N_\pi$ are the number of σ and π electron pairs in each compound respectively. For a set of 50 compounds of hydrocarbons, S, N and O containing compounds, we found σ = -2.36 and π = -0.022 kcal/mol. (For J2P3 method, σ = -1.2 and π = -4.8 kcal/mol) Corrected predictions versus experimental standard heats of formation (298.15 K, 1 atm) are shown to have a RMS deviation for standard heats of formation of 2.11 kcal/mol for a total 50 organic compounds. The original CBHLC corrections are developed targeting oil migration distance indicators such as dibenzothiophenes and methylcarbazoles (only C, H, S and N containing compounds). For this study, the CBHLC method is extended to oxygenates using 14 oxygen-containing compounds (water, 1,4-cyclohexanedione, benzaldehyde, acetone, butanol, 1,2-dihydroxynaphthalene, ethyl decanoate, hexanoic acid, glyoxal, acetaldehyde, butanal, 2,4-pentanedione, hexanal, and decanol)

**Table S3: Quantum calculated heats of formation with and without CBHLC. The experimental heats of formation are included for comparison, and the absolute errors ($\delta H$) are also shown. All values are in kcal/mol**

| | $\Delta H_f^0$ (*exp*)[a] | $\Delta H_f^0$ (*QM*) using eq. 3 - 5 | $\delta H$[e] | CBHLC corrected $\Delta H_f^0$ (*QM*) | $\delta H$[e] |
|---|---|---|---|---|---|
| Water | -57.80 ± 0.0096 | -53.96 | 3.83 | -57.08 | 0.71 |
| Formaldehyde | -25.96 ± 0.5 | -21.82 | 4.14 | -26.42 | -0.46 |
| Acetaldehyde | -40.77 ± 1.50 | -32.40 | 8.38 | -41.96 | -1.19 |
| Acetone | -52.23 ± 0.14 | -39.81 | 12.42 | -54.34 | -2.11 |
| Butanal | -50.61 ± 0.22 | -32.45 | 18.16 | -51.95 | -1.34 |
| Hexanal | -59.38 ± 1.78[b] | -33.13 | 26.25 | -62.56 | -3.19 |
| Glyoxal | -50.64 ± 0.79[c] | -42.60 | 8.04 | -50.65 | -0.01 |
| Ethylene glycol | -94.20 ± 0.67 | -76.74 | 17.46 | -91.77 | 2.43 |
| Hydroxyacetone | -87.42 ± 8.74[b] | -73.89 | 13.52 | -90.40 | -2.98 |
| 2,4-Pentanedione | -91.87 ± 0.31 | -65.46 | 26.41 | -88.41 | 3.46 |
| Glutaraldehyde | -73.49 ± 3.67[b] | -51.05 | 22.44 | -74.00 | -0.51 |
| Cyclopropane carboxylic acid | -80.30 ± 4.01[b] | -57.85 | 22.45 | -78.17 | 2.13 |

a. Experimental values and uncertainties of heats of formation, $\Delta H_f^0$ (*exp*) are obtained from NIST webbook (1). Original references for water (3), formaldehyde (4), acetaldehyde, acetone, and butanal (5), ethylene glycol (6) and 2,4-pentanedione (7)
b. Experimental values heats of formation, $\Delta H_f^0$ (*exp*) are obtained from DIPPR database (8) for hexanal, hydroxyacetone, glutaraldehyde and cyclopropane carboxylic acid.
c. Glyoxal data are obtained from Dorofeeva *et. al.* (9)
d. $\delta H = \Delta H_f^0$ (*QM*) - $\Delta H_f^0$ (*exp*)

**Standard Entropies**. Standard entropies of the molecules from quantum mechanics were used to calculate free energies of formation ($\Delta G^0_f$) and reaction ($\Delta G^0_{rxn}$). Quantum reported gas-phase entropies and experimental entropies (1,8,9) are shown in Table S4.

**Table S4: Reported entropies from quantum mechanics, $S^0_{298K}(QM)$, experimental entropies, $S^0$. Absolute errors ($\delta S$) are shown, and all values are in cal/molK**

| | $S^0$ (exp)[a] | $S^0_{298K}(QM)$ | $\delta S$ [d] |
|---|---|---|---|
| Water | 45.13 ± 0.0024 | 45.085 | -0.05 |
| Formaldehyde | 52.25 | 52.148 | -0.10 |
| Acetaldehyde | 63.04 | 61.813 | -1.23 |
| Acetone | 70.57 | 71.663 | 1.09 |
| Butanal | 82.11 ± 2.46 | 77.901 | -4.20 |
| Hexanal | 100.83 ± 3.02[b] | 89.494 | -11.33 |
| Glyoxal | 65.09 ± 0.72[c] | 64.714 | -0.37 |
| Ethylene glycol | 74.48 | 70.291 | -4.19 |
| Hydroxyacetone | 81.92 ± 8.19[b] | 78.355 | -3.57 |
| 2,4-pentanedione | 86.58 ± 0.87[b] | 91.188 | 4.61 |
| Glutaraldehyde | 97.04 ± 4.85[b] | 88.646 | -8.40 |
| Cyclopropane carboxylic acid | 74.95 ± 2.25[b] | 76.282 | 1.33 |

a. Experimental values and uncertainties of entropies, $S^0$(exp) are obtained from NIST webbook (1). Original references for water (3), formaldehyde (4), acetaldehyde, and acetone (5), butanal (10), ethylene glycol (11).
b. For hexanal, hydroxyacetone, 2,4-pentanedione, glutaraldehyde, and cyclopropane carboxylic acid, $S_f^0$(exp) and the uncertainties are taken from DIPPR database (8).
c. Glyoxal data are obtained from Dorofeeva *et. al.* (9).
d. $\delta S = S^0(QM) - S^0(\text{exp})$

**Standard states conversion.** In order to convert from gas-phase standard condition to solution-phase condition, we can employ the basic equation:

$$\Delta G^{0'} = \Delta G^0 + RT\ln\left(\frac{Q^{0'}}{Q^0}\right) \qquad (9)$$

where $Q$ is the reaction quotient, the ratio of concentrations that appear in the equilibrium constant. For a reaction such as hydration (carbonyl + water = hydrate), the reaction quotient, $Q$, can be written as [hydrate]/[carbonyl][water]. To convert the gas-phase standard state (1 atm) concentration to solution phase standard concentration (1 M), we will define the $Q^{0\prime}$and $\Delta G^{0\prime}$ as values evaluated with all species at 1 atm, while $Q^0$ and $\Delta G^0$ are evaluated in the gas phase with all species at 1M. Assuming the species are ideal gases, their concentrations may be obtained from the ideal gas law as 1/24.5 M (12). For a reaction such as hydration,

$$\Delta G^0(\text{gas, 1M}) = \Delta G^{0\prime}(\text{gas, 1atm}) - RT\ln(24.5) \qquad (10)$$

**Solvation energy.** Solvation energy refers to the change in free energy for a molecular A leaving the gas phase and entering the condensed phase. This free energy can be determined using

$$\Delta G_S^0(A) = \lim_{[A]_{sol} \to 0} \left\{ -RT \ln \frac{[A]_{sol}}{[A]_{gas}}\bigg|_{eq} \right\} \tag{11}$$

When a solute is immersed in a solvent, its charge distribution interacts with that of the solvent (12), and how to treat the solvation effect efficiently and accurately is a long-term challenge in computational chemistry. The solvation model employed in this study is based on the Poisson-Boltzmann (PB) equation.

$$\nabla \varepsilon(\mathbf{r}) \cdot \nabla \phi(\mathbf{r}) - \varepsilon(\mathbf{r}) \lambda(\mathbf{r}) \kappa^2 \frac{k_B T}{q} \sinh\left[ \frac{q\phi(\mathbf{r})}{k_B T} \right] = -4\pi\rho(\mathbf{r}) \tag{12}$$

The charge density $\rho$ of the solute may be expressed as some continuous function of **r**. $\varepsilon$ is the dielectric constant of the medium, $\phi$ is the electrostatic potential, $\lambda$ is the simple switching function with is zero in regions inaccessible to electrolyte and one otherwise. $q$ is the charge of the electrolyte ions, and $\kappa^2$ is the Debye-Hückel parameter given by

$$\kappa^2 = \frac{8\pi q^2 I}{\varepsilon k_B T} \tag{13}$$

where $I$ is the ionic strength. Solving the PB equation can be quite complicated and usually involves additional assumptions. At low ionic strength it is given as a linearized PB equation using a truncated power expansion for the hyperbolic sine,

$$\nabla \varepsilon(\mathbf{r}) \cdot \nabla \phi(\mathbf{r}) - \varepsilon(\mathbf{r}) \lambda(\mathbf{r}) \kappa^2 \phi(\mathbf{r}) = -4\pi\rho(\mathbf{r}) \tag{14}$$

The solvation model in this study is limited by zero ionic strength, the PB equation can be reduced to Poisson equation and can be solved relatively easier. Details of the computational procedure of the solvation model in this study can be found in the original reference Tannor *et. al*. (13).

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